

ATOMS IN STATIC FIELDS: CHAOS OR DIFFRACTION ?

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A brief review of the manifestations of classical chaos observed in atomic systems is presented. Particular attention is paid to the analysis of atomic spectra by periodic orbit-type theories. For diamagnetic non-hydrogenic Rydberg atoms, the dynamical explanation for observed spectral features has been disputed. By building on our previous work on the photoabsorption spectrum, we show how, by the addition of diffractive terms, the spectral fluctuations in the energy level spectrum of general Rydberg atoms can be obtained with remarkable precision from the Gutzwiller trace formula. This provides further evidence that non-hydrogenic systems are most naturally described in terms of diffraction rather than classical chaos.

1 Atoms as Laboratories of Quantum Chaos

Atomic physics has provided some of the most important examples of real, experimentally observable, quantum systems for which the underlying classical motion is chaotic. In broad terms, the study of chaos in atoms comprises two major strands. One is the study of time-dependent periodically driven systems where the phenomenon of dynamical localization provides a mechanism for the quantum suppression of chaotic diffusion. This is exemplified by the behaviour of hydrogen in a microwave field¹ and, more recently, atoms in traps.² The other strand is the study of time independent systems. Here, highly excited atoms in static external fields have received particular attention. Although chaos in the sense of exponential sensitivity to perturbations is not present, atomic spectra exhibit the characteristic ‘footprints’ of classical chaos, such as eigenvalue statistics similar to those of random matrices, spectral modulations and ‘scarring’ of wavefunctions by unstable periodic orbits.

The classic 1969 Garton-Tomkins spectrum of barium in a magnetic field³ revealed the first ‘footprints’ of classical orbits in the quantum spectrum of a ‘real’ system. Oscillations observed in the $m = 1$ spectrum near the ionization limit at energy spacing $\sim 1.5\hbar\omega$ were, much later, associated with the periodic orbit perpendicular to the magnetic field. In Fig. 1 we show the Garton-Tomkins spectrum. Above are shown Wigner functions and classical Poincaré surfaces-of-section for diamagnetic hydrogen in three different regimes of energy. The Wigner functions show three different stages of the Garton-Tomkins orbit: (a) scar, (b) bifurcation and (c) torus quantization. The surfaces-of-section show the gradual transition from regularity to chaos as

the scaled energy increases.

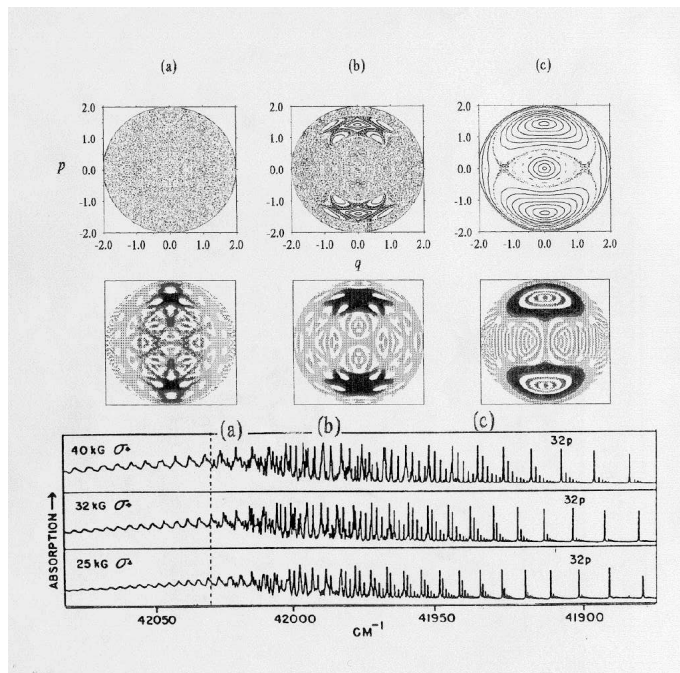


Figure 1: The classic Garton-Tomkins spectrum of barium in a magnetic field. Above are shown are Wigner functions and classical Poincaré surfaces-of-section for diamagnetic hydrogen at scaled energies (a) $\varepsilon = -0.1$, (b) $\varepsilon = -0.316$ and (c) $\varepsilon = -0.5$ showing the gradual transition to chaos as ε increases.

Such is the experimental resolution now obtainable (being typically of the order of 50MHz) that atoms still provide one of the best ‘laboratories’ for investigating and testing theories of ‘quantum chaology’, although there is also now great interest in chaos in mesoscopic devices.

For an atom in a strong external field the typical spectrum, involving highly excited states in the classically chaotic regime, looks extremely irregular. Eigenstates generally defy any form of classification in terms of quantum numbers. However, in the semiclassical limit ($\hbar \rightarrow 0$) periodic orbit theory, in the guise of the Gutzwiller Trace Formula (GTF),⁴ exposes the beautiful connection between modulations in the quantum spectrum and classical orbits. Because of a useful scaling property, Fourier transforms of calculated atomic spectra can be related directly to classical stabilities. Hence the GTF has pro-

vided atomic physicists with an extremely powerful framework for the analysis of quantum spectra in the classically chaotic limit.

However it is not widely appreciated that there exist two separate semiclassical theories for the analysis of atomic spectra. The GTF relates classical periodic orbits to oscillations in the *energy level* spectrum in the semiclassical regime. *Closed orbit* theory^{5,6} on the other hand, is the appropriate tool for the investigation of experimental *photoabsorption* spectra (which involve a quantum spectrum weighted by the appropriate absorption probability).

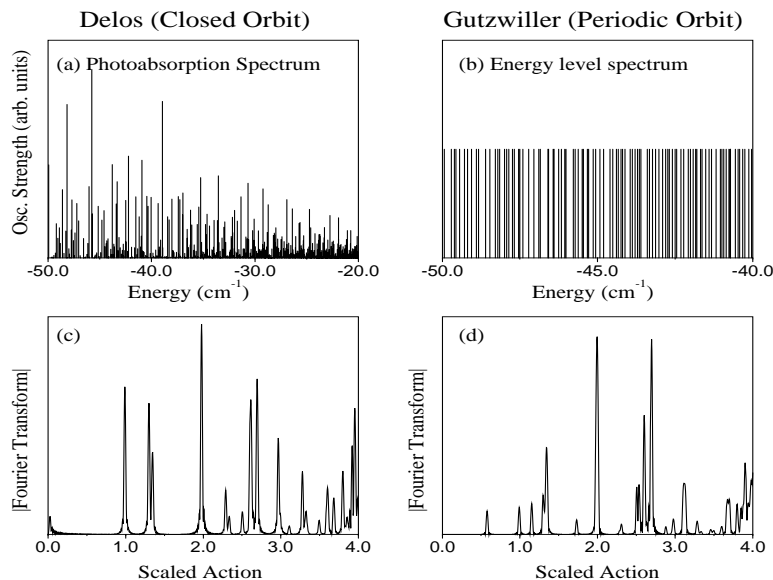


Figure 2: Comparison between calculated $m = 0$, even parity (a) photoabsorption and (b) energy level spectra for diamagnetic hydrogen. (c) and (d) show the corresponding Fourier transforms which reveal the periodicities in the spectral modulations. Note in particular the differences in the heights of the peaks and the additional modulations seen in the energy level spectrum case.

There are important differences between the two theories which are illustrated qualitatively in Fig. 2. These become especially significant when we seek to understand the differences in behaviour between hydrogen and other atoms. These differences in behaviour have been given different dynamical interpretations by different authors. We review first the main arguments concerning non-hydrogenic spectra, before contrasting closed orbit theory with periodic orbit theory.

2 Chaos Versus Diffraction in Non-Hydrogenic Atoms

It is now 10 years since it was first shown that the GTF provides a quantitative description of highly excited hydrogen atoms in strong external fields.⁷ However, comparisons between accurate quantal spectra reveal spectral amplitudes for non-hydrogenic atoms that differ substantially from those of hydrogen together with additional modulations that cannot be associated with any hydrogenic orbits.^{8,9} Hence, it has been a long-standing problem to apply the GTF to other species of singly excited (Rydberg) atoms.

Theoretical calculations⁹ found the differences between hydrogen and other diamagnetic atoms to be most marked in the low energy regime where hydrogen is regular. Here, non-hydrogenic atoms show many ‘footprints’ of chaos. For example, spectral statistics lie close to the Wigner (chaotic) limit,^a suggesting underlying chaotic classical motion. However, quantum phase-space distributions (Wigner functions) do not have the more ‘ergodic’ appearance of those of hydrogen in the classically chaotic regime. Instead, torus-like structures are found but with each eigenstate now linked to several ‘tori’ rather than just one as in the hydrogenic case; clearly this is not the signature of underlying classical chaos.

In 1994, the additional spectral modulations (‘core-scattered’ peaks) seen for non-hydrogenic atoms were in fact observed experimentally by three separate groups^{11,12,13} and identified¹² as arising from combinations of hydrogenic orbits.

Some progress towards the goal of adapting the GTF to describe all atoms was made in 1995 when we successfully adapted the related closed orbit theory of Delos and co-workers,^{5,6} which describes the experimentally measured *photoabsorption* spectrum, to general non-hydrogenic atoms.^{14,15} However, this work gave only limited insight and little qualitative explanation of the role played by the non-hydrogenic core in the actual *energy level* spectrum.

Classical calculations using a model potential to describe the effect of the ionic core^{11,16,17} suggest one possible explanation, namely that the presence of the core drastically destabilizes the classical motion. This gives rise not only to a reduction in amplitude of the oscillations associated with classical hydrogenic orbits but also to a multitude of new orbits not found in the hydrogenic problem. Although this approach provides physical insight into the effect of the ionic core, quantitative agreement is generally poor, even failing to reproduce the quantum results for smaller atoms such as helium.¹⁸ Indeed, any sort of classical description of the core-scattering process may be questionable for atoms such as helium or lithium, where only one or two partial waves are

^aThis has been recently verified by experiment.¹⁰

influenced by the core.

Our 1995 work suggested an alternative explanation of these phenomena. In non-hydrogenic atoms both the size of the core and the characteristic de Broglie wavelength are of the order of 1 au. Thus it is more natural to describe core effects in terms of a *diffractive* process rather than classical paths and their stability parameters. (Recall that diffraction occurs when an obstacle is encountered whose size is smaller than the wavelength of the incident wave.)

There is now new evidence that this is indeed the case. Now,¹⁹ we have shown that spectral fluctuations of general Rydberg atoms are given with remarkable precision (to within 1%) on including diffractive corrections to the GTF. Several previously unknown features in the non-hydrogenic energy level spectra were found. There are additional modulations that are neither periodic orbits nor combinations of periodic orbits. Also, while ‘core-shadowing’ generally decreases the amplitude of oscillations associated with primitive periodic orbits it can also lead to increases. In addition, the spectral statistics of diamagnetic non-hydrogenic atoms, previously thought to lie at the Wigner limit, have been found²⁰ to belong to an entirely new generic distribution (‘Half-Poisson’) usually associated with diffractive systems.

3 Closed Orbit Theory Versus Periodic Orbit Theory

3.1 Closed Orbit Theory

Closed orbit theory has been presented elsewhere in great detail^{5,6} so we give only an outline. Briefly, when an atom absorbs a photon, the electron propagates outwards in a near zero-energy Coulomb wave. At sufficiently large distances from the nucleus the wave propagates semiclassically along classical trajectories. Eventually, the trajectories and their associated waves are turned back by the action of the external field. Some of the trajectories return to the vicinity of the nucleus and the waves associated with them interfere with the outgoing waves generating oscillations in the absorption spectrum. The result is a formula for the average oscillator-strength density that can be written as a combination of a smooth background plus an oscillatory term,

$$f_{\text{osc}}(E) = \text{Im} \sum_n \sum_k C_k^n(E) \exp[i(S_k^n(E)/\hbar - \pi\mu_k^n/2 - 3\pi/4)], \quad (1)$$

which arises from the interference of semiclassical waves associated with closed orbits of an electron of energy E . Each different orbit is indexed by k and the repetitions of each orbit are labelled by n . The ‘recurrence amplitude’, $C_k^n(E) \propto m_{12}^{-1/2}$, contains information about the stability of the orbit via the m_{12} element of the stability matrix, M ; this is obtained by studying the

classical motion in the neighbourhood of the orbit. The phase depends on the classical action, $S_k^n = n \oint_k \mathbf{p} \cdot d\mathbf{q}$, plus an additional term that is computed from the Maslov Index, μ_k^n , and other geometrical considerations.

Whereas closed orbit theory describes the *photoabsorption* spectrum in terms of the properties of classical orbits that *close* at the nucleus, the Gutzwiller Trace Formula⁴ relates periodicities in the quantum *density of states*, $\rho(E) = -(1/\pi)\text{Im Tr } G(E)$, to isolated *periodic* orbits. In the semiclassical limit ($\hbar \rightarrow 0$) $\rho(E)$ can also be written as the sum of a smooth background term together with an oscillatory part of the form,

$$\rho_{\text{osc}}(E) = -\frac{1}{\pi} \text{Im} \sum_p \frac{T_p(E)}{i\hbar} \sum_n \frac{\exp[i(S_p^n(E)/\hbar - \mu_p^n \pi/2)]}{|2 - \text{Tr } M_p^n|^{1/2}}, \quad (2)$$

where S_p^n again denotes the classical action, T_p the period, and μ_p the Maslov index and M_p^n the stability matrix for the n th repetition of the p th periodic orbit.

Although Eqs (1) and (2) show that the periodicity of the spectral modulations is the same for both theories there are important differences. Firstly, the sum in Eq. (1) only includes contributions from orbits which deliver amplitude back to the vicinity of the well-localized initial state: only orbits that return to the nucleus contribute. Note that these orbits need not be periodic. For the GTF, *all* periodic orbits of the classical system contribute to the sum in Eq. (2). Secondly, the amplitudes of the contributions are different. Both formulae contain information about the stability of the orbit via the stability matrix, M . However, for closed orbit theory, the recurrence amplitude is related to m_{12} —an off-diagonal element of M —while in the GTF, the amplitude of the modulation due to a given orbit is proportional to $(2 - \text{Tr } M)^{-1/2}$.

3.2 Gutzwiller Trace Formula with Diffraction

The periodic orbit theory of diffraction was developed recently for Hamiltonians with discontinuities.^{21,22} For such systems, periodic orbits are decomposed into two types: those that do not intersect the discontinuity (*geometric* orbits) and those that do (*diffractive* orbits). The density of states is then obtained as a sum:

$$\rho(E) = \underbrace{-\frac{1}{\pi} \text{Im Tr } G_g(E)}_{\text{geometric}} - \underbrace{\frac{1}{\pi} \text{Im Tr } G_D(E)}_{\text{diffractive}}. \quad (3)$$

Taking the trace over the first (geometric) term yields the well-known GTF. The trace over the second (diffractive) contribution has been shown to be^{21,22}

$$\text{Tr } G_D(E) = \sum_p \frac{T_p}{i\hbar} \prod_n d(n) G(q_n, q_{n+1}; E), \quad (4)$$

where T_p is the total sum of periods taken over the paths between the vertices and $d(n)$ is the diffraction constant which depends on the type of diffraction. Equation (4) encapsulates the important result that the trace integral taken between the n th and $n + 1$ th diffractive points is proportional to the Green's function between those points.

3.3 Application to Non-Hydrogenic Atoms

We now wish to apply the diffractive periodic orbit theory in an atomic context by treating the non-hydrogenic core as a diffractive source. The crucial step is to obtain an expression for the diffractive constant $d(\theta_i, \theta_f)$.

Consider a wave incident on the atomic core at an angle θ_f to the z -axis. On reaching the core, this wave produces a scattered wave, ψ_{scatt} , which feeds outgoing semiclassical waves along periodic orbits; this scattered wave can be decomposed into two components:⁶

$$\psi_{\text{scatt}}(r, \theta) = \underbrace{\psi_{\text{Coul}}(r, \theta \simeq \theta_i)}_{\text{Coulomb-scattered}} + \underbrace{\psi_{\text{core}}^{\theta_f}(r, \theta)}_{\text{Core-scattered}}. \quad (5)$$

The Coulomb-scattered wave, ψ_{Coul} , is strongly back-focussed and equated with the source for geometric paths. The core-scattered wave, ψ_{core} , on the other hand, is equated with the source of diffractive semiclassical waves. At some radius r_0 , we express ψ_{core} in a partial wave expansion which, for $m = 0$, is⁶

$$\psi_{\text{core}}^{\theta_f}(r_0, \theta) = \left(\frac{2\pi^2}{r_0^3} \right)^{\frac{1}{4}} \sum_{l=0}^{\infty} Y_{l0}^*(\theta_f, 0) Y_{l0}(\theta, 0) (e^{2i\delta_l} - 1) e^{i(\sqrt{8r_0} - 3\pi/4)} \quad (6)$$

where δ_l indicates a set of l -dependent quantum defects describing the non-hydrogenic core. Finally, we take d to be the fractional amplitude scattered by the core:

$$d(\theta_i, \theta_f) = \psi_{\text{core}}^{\theta_f}(r_0, \theta_i) / \psi_{\text{Coul}}(r_0, \theta_f). \quad (7)$$

For small atoms only the lowest partial waves have non-zero quantum defects and hence contribute to the sum in Eq. (6). For example, for even

parity lithium, $\delta_0 \simeq 0.4\pi$ and $\delta_{l \geq 2} \simeq 0$. For such s -wave scattering, $\psi_{\text{core}}^{\theta_f}$ is isotropic. All our calculations have been carried out for the case of s -wave scattering so below $\delta \equiv \delta_{l=0}$; generalization to odd parity spectra and atoms with more than one non-zero quantum defect is straightforward.

For the case of s -wave scattering, each diffractive contribution in Eq. (4) is:

$$dG = \hbar^{1/2} (e^{2i\delta} - 1) \left| \frac{2\pi}{m_{12}} \sin \frac{\theta_i}{2} \sin \frac{\theta_f}{2} \right|^{1/2} e^{i(S/\hbar - \mu\pi/2 - \pi/4)} \quad (8)$$

and, in effect, represents the contribution of a pure diffractive orbit. Note the additional phase of $-\pi/4$ relative to an equivalent primitive geometric periodic orbit. Eq. (8) supersedes an expression given previously¹⁸ which merely gave an estimate of the fractional reduction in amplitude for R_1 .

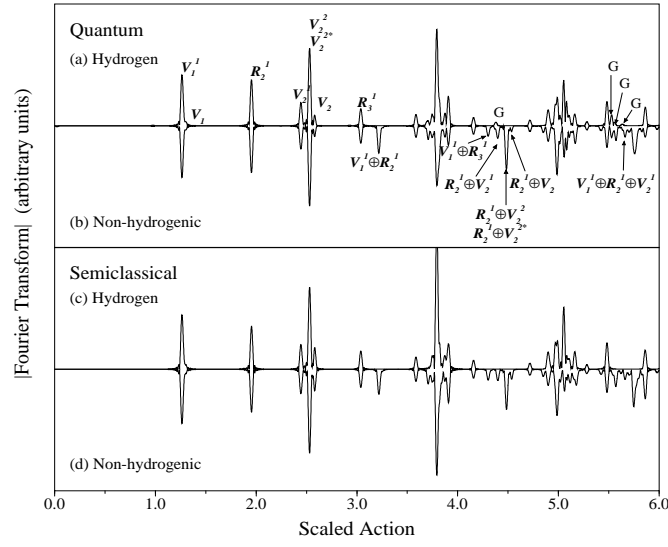


Figure 3: (a) Comparison of Fourier transforms of the density of states for hydrogen and a non-hydrogenic atom with $\delta = 0.5\pi$ in a static magnetic field from a fully quantal calculation with average $\hbar = 1/90$ at $\epsilon = -0.2$. (b) Comparison between quantal and semiclassical difference spectra obtained by coherently subtracting the Fourier transforms shown in (a).

In Fig. 3(a) we show Fourier transforms of the oscillatory part of the even- l , $m = 0$, eigenvalue spectra for hydrogen and a non-hydrogenic atom with $\delta = 0.5\pi$ in a static magnetic field at scaled energy $\epsilon = -0.2$ and $n = \gamma^{-1/3} = \hbar^{-1}$ ranging from 60 to 120, so the average value of $\hbar^{-1} = 90$. In Fig. 3(b) we plot the difference spectrum obtained by coherently subtracting the Fourier

transform of the hydrogenic spectrum from that of the non-hydrogenic; this exposes the diffractive contributions and eliminates contributions from periodic orbits which do not pass through the core. For comparison, we also plot a semiclassical difference spectrum obtained by summing all terms of order $\sqrt{\hbar}$ and \hbar ; agreement is excellent. The discrepancy in D_2 is due to the effects of bifurcations that are not taken into account in the semiclassical calculation presented here.

We can see that for the non-hydrogenic case the amplitudes of the Garton-Tomkins orbit, R_1 and its harmonic R_2 , as well as the balloon, V_1^1 , and other orbits are substantially reduced. There are additional small peaks which correspond accurately to sums of periodic orbits. Importantly, there are strong peaks (marked D_1 and D_2) which do not match any combination of orbits. At these scaled actions ($S \simeq 2.87$ and $S \simeq 2.94$) we find orbits that are closed but not periodic. For hydrogen, only orbits that are periodic can contribute. Here we see that pure diffractive orbits, such as D_2 , can contribute to the non-hydrogenic spectrum at $O(\sqrt{\hbar})$ so are substantially stronger than combinations of orbits. The peak at $S \simeq 2.87$ is due to an isolated closed orbit and is obtained almost exactly from Eq. (8) as seen in Fig. 3(b) (note that in Fig. 3(a) the peak associated with this orbit is masked by the peak of a periodic orbit which does not approach the nucleus). The peak at $S \simeq 2.94$ consists of contributions from a pair of non-isolated orbits close to a bifurcation so their contribution is over-estimated semiclassically. On examination of the diffractive orbits we find that they correspond to the first closure of asymmetric periodic orbits, some of which correspond to the X_n series of ‘exotic orbits’.²³ In hydrogenic eigenvalue spectra such orbits can only contribute at their *full period*, whereas in the diffractive case they appear at *closure*.

4 Conclusions

We have now successfully extended our 1995 study of closed orbit theory and for non-hydrogenic spectra to a study of periodic orbit theory *per se*, in the form of the Gutzwiller trace formula. We have carried out a detailed study of diffraction in atoms in the GTF for several scaled energies to study the \hbar and δ dependence of the diffractive effects. We find that, away from bifurcation effects, our simple diffractive corrections describe the quantal spectra to within an accuracy of about 1%. We note that a model-potential simulation with fully chaotic dynamics gives agreement only to within a factor of about two in general. We conclude that since the atomic core is of the order of one atomic unit, the diffractive effect is too weak to be simulated accurately by the cumulative effect of numerous unstable orbits. However, for low energy, it is

most naturally and accurately described as a combination of stable motion, coupled with a breakdown of the usual semiclassics due to diffraction.

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